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Synthesis and properties of new clay-reinforced aromatic polyimide/nanocomposite-based 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 1,3-bis(4-aminophenoxy)propane

Abstract: A series of poly(imide-ether)-clay nanocomposite materials-based 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 1,3-bis(4-aminophenoxy)propane and layered sodium montmorillonite (MMT/Na^+) clay were successfully prepared by *in situ* reaction through thermal imidization up to 200°C. Poly(amic acid) (**6**) was prepared through the reaction of 1,3-bis(4-aminophenoxy)propane (**4**) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**5**), and then a thermal plan of imidization was used for the synthesis of nanocomposite materials. The resulting nanocomposite films containing 0.5, 1, 3, and 5 wt.% of organoclay were characterized by Fourier transform infrared spectroscopy, wide-angle powder X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis, respectively. The introduction of organoclay in the polymer resulted in improved thermal stability.

Keywords: flexible moieties; nanocomposite; organoclay; poly(imide-ether).

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1 Introduction

Nanocomposite is a class of composite in which the reinforcing phase dimensions are in the order of nanometers. Because of their nanometer size characteristics, nanocomposites possess superior properties than the conventional microcomposites due to maximizing the interfacial adhesion. Nanostructured composites based on polymer and layered silicates typically exhibit properties far superior to those of separate component, which make them extremely interesting in the field of design and creation of new construction materials [studies on thermal and mechanical polyimide (PI) clay]. In the last decade, the properties of a variety of elastomers, linear or crosslinked polymers, have been improved by the incorporation of layered silicates. Several studies revealed that the inclusion of clay mineral enhanced the mechanical properties of both rigid and flexible polymer systems.

Aromatic PIs are widely employed in the aerospace, microelectronics, optoelectronics, and composites industries because of their excellent balance of thermal and mechanical properties. However, their applications have been limited in some fields because the aromatic PIs are normally insoluble in common organic solvents and have extremely high glass transition or melting temperatures. It is well known that the chemical composition and chain structure of aromatic PIs were responsible for their prominent properties and responsible for their poor processibility [1]. PIs are types of high performance polymeric materials that have been widely used in the aerospace, electronics, and microelectronic industries because of their outstanding thermal and chemical stabilities, mechanical properties (e.g., high tensile strength and modulus), electrical properties (e.g., low dielectric properties), and radiation resistance [2–6]. Continuing research interests are devoted to further improving the performance of PIs in some specific applications [7–9]. For example, PIs can be used as a key component of the facemask, the constructive material of a membrane that allows the air to go through but precludes the dust or harmful gas in case of a fire, or used in other filtering and separating applications requiring high performances [10–12]. Natural sodium montmorillonite (MMT/Na^+) consisted of layered silicates carrying negative charges that formed ionic bonds with metal cations in interlayer of the clay [13]. The layered silicates used in these materials belong chemically to the family known as 2:1 phyllosilicates [14]. The chemical structure of MMT/Na^+ used for polymer-clay nanocomposites (PCN) preparation

consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either magnesium or aluminum hydroxide. The Na^+ and Ca^{2+} present in the interlayer regions can be replaced by organic cations such as alkyl ammonium ions through a cationic-exchange reaction to render the hydrophilic silicate layer organophilic, leading to the development of PCN materials [15]. It is necessary to modify the surface chemistry of MMT by replacing inorganic cations in the inner layer of silicates with various organic cationic molecules. The surface modification of the layered silicates increased interlayer spacing and became more uniform after intercalation with organic molecules. This surface treatment with organic molecules made MMT more miscible with polymer molecules. Thus, polymer molecules are allowed to enter the enlarged interlayer of organoclay for further intercalation or exfoliation [16–19].

In the present work, for the first time, we wish to report the synthesis and characterization of new nanocomposites of PI with organoclay, which have been synthesized using *in situ* intercalation technique. PI was prepared by reacting 1,3-bis(4-aminophenoxy)propane with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride in dimethylacetamide (DMAC). PI chains diffused into the space between the organoclay layers. Nanocomposite films containing 0.5, 1, 3, and 5 wt.% of organoclay obtained by evaporation of the solvent were characterized by Fourier transform infrared (FTIR) spectroscopy, wide-angle powder X-ray diffraction (XRD), and scanning electron microscopy (SEM).

The effects of material composition on the thermal stability of bulk PI and PCN materials were studied by thermogravimetric analysis (TGA). The aim of the present study was to synthesis a class of high-temperature polymer nanocomposite materials by using a new polymer.

2 Experimental

2.1 Materials

All chemicals were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), and Merck Chemical (Darmstadt, Germany). The organically modified clay (cloisite 20A) used in the preparation of nanocomposite films was modified with benzidine. This organoclay consists of a 95 mEq/100 g MMT/Na^+ modified with a quaternary ammonium salt that contains a long-chain hydrocarbon tallow group.

2.2 Techniques

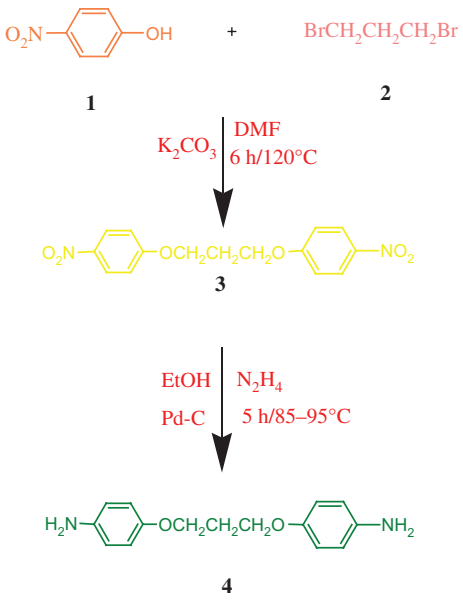
^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz instrument (Bremen, Germany). FTIR spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid were performed by using KBr pellets. Vibration transition frequencies were reported in wave number (cm^{-1}). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Elemental analyses were performed by Vario EL equipment. Wide-angle XRD study of the samples was performed with a X'pert pw 3064 XRD with a copper target at a scanning rate of 4° min^{-1}. The morphologies of the fractured surfaces of the extrusion samples were investigated using a LEO 1455 VP SEM. TGA data for polymers were taken on a Mettler TA4000 System under N_2 atmosphere at rate of 10°C min^{-1}.

2.3 Synthesis of diamine monomer 4

The diamine was synthesized through the aromatic nucleophilic substitution of corresponding with 4-nitrophenol (**1**) and 1,3-dibromopropane (**2**) in the presence of potassium carbonate followed by catalytic reduction with hydrazine monohydrate 10% Pd/C. The procedure was as follows: a solution of 4-nitrophenol (**1**) (2 g, 14.40 mmol), 1,3-dibromopropane (**2**) (7.20 mmol), potassium carbonate (1 g, 7.20 mmol), and *N,N*-dimethylformamide (10 ml) was refluxed for 6 h at 120°C. The mixture was precipitated in an ice-water mixture, and the crude dinitro intermediate was recrystallized from ethanol (96%), affording 2.12 g (69%) of yellow whitish solid (**3**), m.p.: 133–134°C, FTIR (KBr, cm^{-1}): 3058 (w), 1609 (s), 1534 (s), 1411 (m), 1348 (s), 1181 (s), 1111 (s), 987 (s), 852 (s), 756 (m), 702 (s), 543 (m) cm^{-1}. H-NMR (300 MHz, DMSO-d_6, TMS): δ; 8.17–8.20 (t, 4H), 7.12–7.15 (t, 4H), 4.19 (t, 4H), 1.92 (s, 4H) ppm.

A solution of the obtained dinitro compound (1 g, 5.17 mmol), 0.5 g of 10% Pd on active carbon (10% Pd/C), and 200 ml ethanol was added dropwise to hydrazine monohydrate (15 ml) at 85°C and then refluxed for 5 h. The mixture was filtered to remove 10% Pd/C, and the filtrate was poured into water and dried to afford 1 g (83%) (**4**). m.p.: 109–111°C, FTIR (KBr, cm^{-1}): 3058 (w), 1609 (s), 1534 (s), 1411 (m), 1348 (s), 1181 (s), 1111 (s), 987 (s), 852 (s), 756 (m), 702 (s), 543 (m) cm^{-1}. ^1H-NMR (300 MHz, DMSO-d_6, TMS): δ; 8.17–8.20 (dd, 4H), 7.12–7.15 (dd, 4H), 4.19 (s, 4H), 1.92 (s, 4H) ppm.

The flowchart of the reaction is listed as Scheme 1.



Scheme 1 Synthesis of diamine **4**.

2.4 Preparation of PI film through thermal imidization

A typical procedure to prepare PI film by thermal imidization was as follows: amounts of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (0.322 g, 1 mmol) (cup A) and 1,3-bis(4-aminophenoxy)propane (0.5 g, 1 mmol) (cup B) were dissolved separately in 3 ml DMAC stirring for 1 h under N_2 atmosphere at room temperature. Cup B was introduced into cup A followed by stirring at room temperature for 24 h to form the PAA. The resulting PAA solution was cast onto a glass and placed in an oven for a programmed heat treatment: 30 min at 80°C, 1 h at 110°C, 2 h at 170°C, and 3 h at 200°C.

2.5 Preparation of organically modified layered silicates

Organically modified layered silicates were synthesized by a cation exchange reaction between MMT/Na^+ and the ammonium salt of benzidine. Then, 5 g MMT/Na^+ was dispersed in 600 ml water. The amount of modifier was dissolved in water and a stoichiometric amount of concentrated HCl was added to the solution. Dissolved clay was added to the solution of the modifier and this mixture was agitated vigorously for 3 h. The blackish gray precipitates were isolated by suction filtration and washed with 400 ml hot water. This process was repeated thrice to ensure the removal of excess ammonium salt of benzidine diamine, thus ensuring complete removal of chloride ions. The final product obtained by filtration was dried in a vacuum oven for 24 h.

2.6 *In situ* polymerization of PCNs by thermal imidization

A procedure for the preparation of PCNs by thermal imidization is shown in Scheme 2. An appropriate amount of organoclay (0.5, 1, 3, and 5 wt.%) was introduced into 3 ml DMAC with stirring for 24 h at room temperature (cup A). Then, 1 mmol dianhydride was dissolved in 1.5 ml DMAC with stirring for 20 min (cup B). Cup B was introduced into cup A and stirred for 24 h at room temperature. Then, 1 mmol diamine was dissolved in 1.5 ml DMAC with stirring for 10 min at room temperature under N_2 atmosphere (cup C). Cup C was introduced into cup (A+B) for 24 h at room temperature under N_2 atmosphere to form the PAA. The resulting solution was then cast onto a glass plate and heat treated in a high-temperature oven with the same program as that for the PI film.

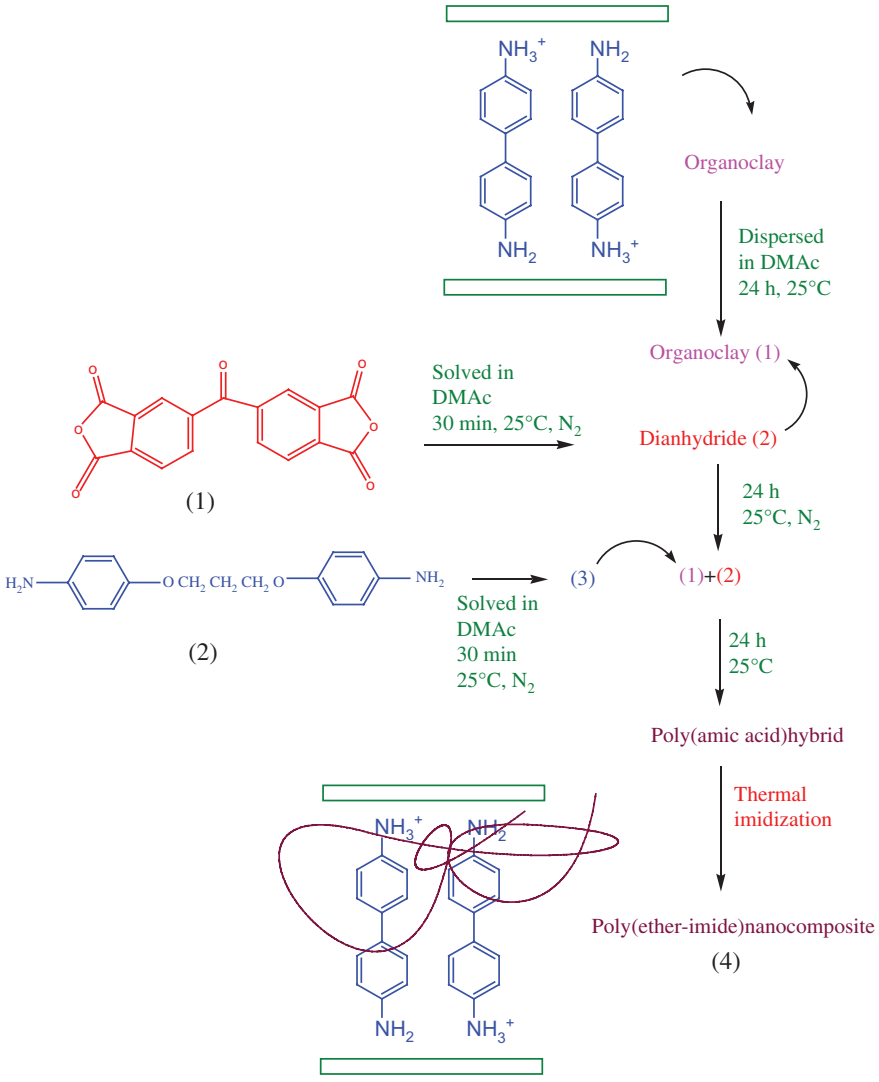
3 Results and discussion

3.1 Characterization

^{1}H-NMR spectrum of diamine (**4**) that showed peaks at 2.15–2.20 ppm assigned to H (a) related to diamine protons. Also, a broad singlet peak at 3.41 ppm was assigned to the H (b) protons of the NH_2 groups. Peaks at 4.05–4.09 ppm were assigned to H (c) related to 4H of CH_2 near oxygen. Peaks at 6.74–6.78 and 6.62–6.65 ppm showed doublet of doublet, which was assigned to the H (d) and H (e) aromatic protons (Figure 1).

3.2 XRD

Figure 2 illustrates the wide-angle powder XRD patterns of organoclay, PI, and a series of PCN materials. Raw clay was found to show a diffraction peak at $2\theta=9.92°$ (d-spacing=0.89 nm). In this spectrum, the d-spacing of organoclay based on Bragg's law ($n\lambda=2d\sin\theta$) at $2\theta=6.78°$ was 1.30 nm. Also, the XRD curves of PCNs containing 0.5, 1, 3, and 5 wt.% of organoclay did not display any XRD peak at $2\theta=2–10°$, indicating that the d-spacing of silicate layers had been either intercalated or the silicate layers were exfoliated completely in PI matrix.



Scheme 2 Synthesis of nanocomposite **8**.

3.3 SEM

Figure 3(A–C) shows clay phases within the nanocomposite films with organoclay contents of 1%, 3%, and 5%. The PCN1, 3, and 5 was well dispersed in a continuous PI phase. A comparison of the micrographs reveals that the fractured surfaces of the hybrid films with higher clay contents were more deformed than those of the films with low clay contents.

3.4 TGA

Thermal stability of the nanocomposites was determined by thermogravimetric technique under N_2 atmosphere at a heating rate of 10°C min^{-1}. Thermograms obtained for these materials are shown in Figure 4. The TGA results of PI, PCN1, and PCN5 are summarized in Table 1. The increase in thermal stability of these hybrids with an increasing clay loading was likely due to two factors [20]: (1) the significant effect of small amounts of dispersed clay layers on the free volume of the PI and (2) the confinement of intercalated polymer chains within the clay galleries, which prevented the segmental motions of the chains. Similar results have been obtained in other studies of polymer nanocomposites [21, 22].

Thermal decomposition temperatures of the PI, PCN1, and PCN5 are between 400°C and 455°C. TGA results indicated that these materials were found thermally stable, which increases with the addition of clay content in the polymer matrix. The increase of PCN5 in

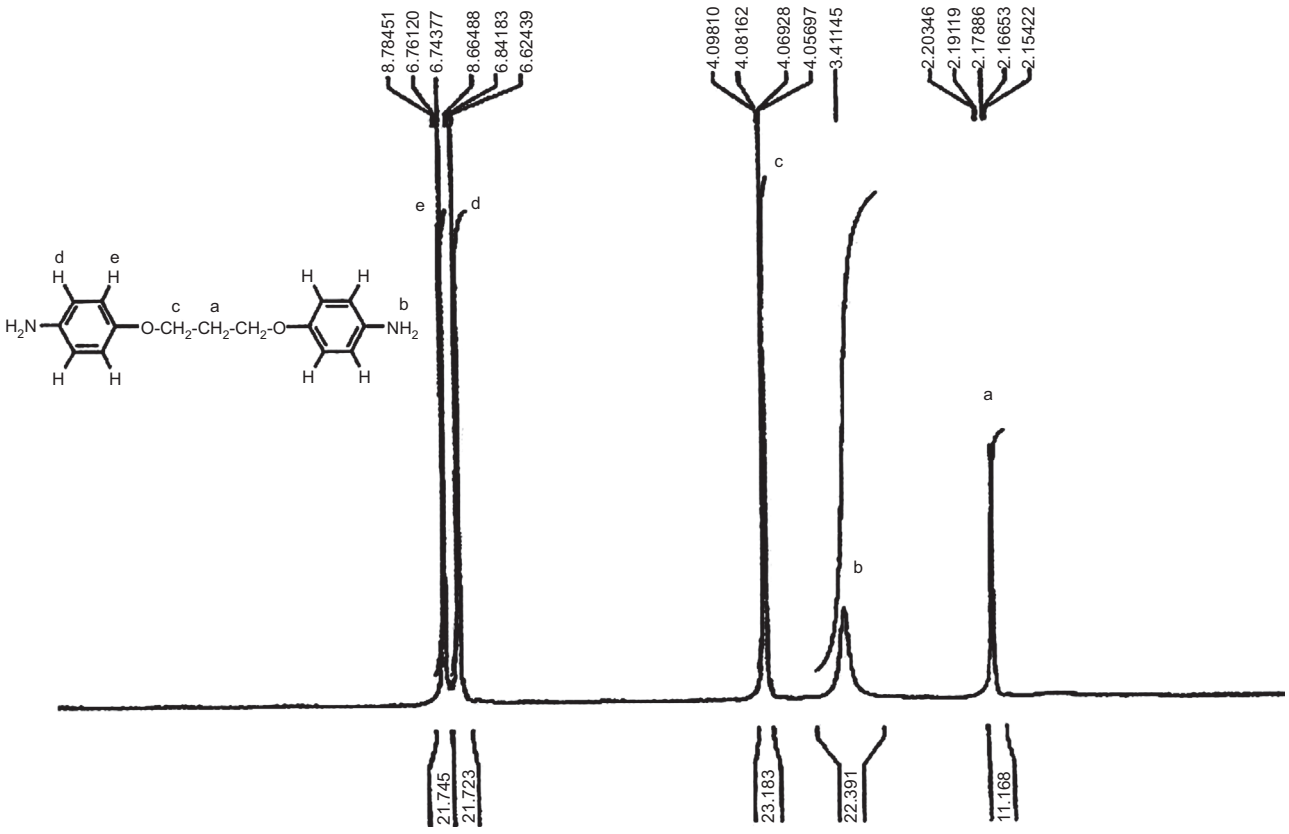


Figure 1 ^{1}H-NMR spectrum of diamine **4**.

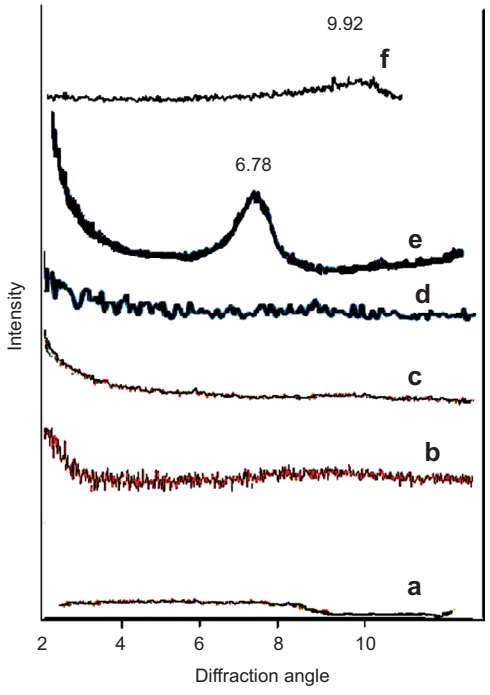


Figure 2 Wide-angle powder XRD patterns for PCN0.5, PCN1, PCN3, PCN5, organoclay, and MMT/Na^{+}.

the thermal stability may result from the high thermal stability of organoclay network and the physical crosslink points of the organoclay particles, which limited the movement of the molecular chain of polymer. PCN1 thermal stability decrease a little because of agglomeration of organoclay particles. The weight retained by these samples at 800°C was roughly proportional to the amount of organoclay in the nanocomposites. Organoclay was found to increase the thermal stability presumably due to superior insulating characteristics of the layered silicate acting as mass transport barrier to the volatile products generated during decomposition. The char yield can be a decisive factor to estimate the limited oxygen index (LOI) of PI, PCN1, and PCN5 according to the Van Krevelen-Hoftyzer's equation [23]:

$$LOI=17.5+0.4\ CR,$$

where CR is the char yield. PI, PCN1, and PCN5 had LOI values 30.3, 36.7, and 34.5, respectively, which were calculated from their char yield. Based on the LOI values, such macromolecules can be classified as self-extinguishing PI and PCNs.

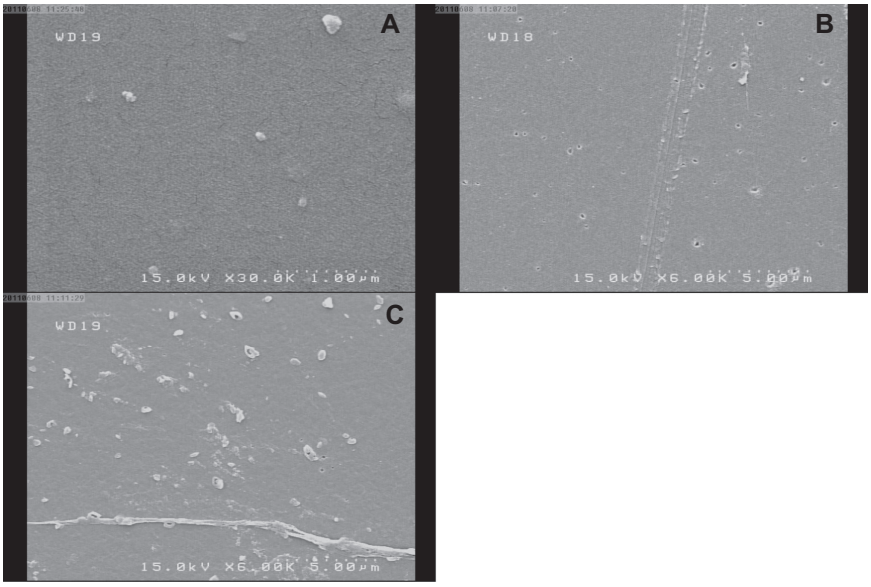


Figure 3 SEM images shown in (A) PCN1%, (B) PCN3%, (C) PCN5%.

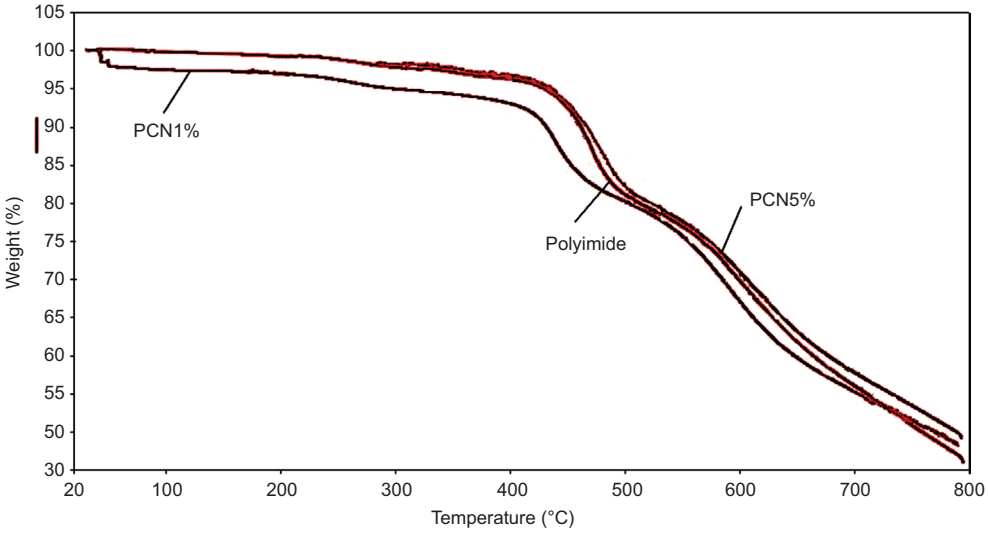


Figure 4 Comparison between thermal gravimetric thermograms of PI, PCN1%, and PCN5%.

Table 1 Thermal behavior of PI, PCN5, and PCN10.

Compound	Feed composition		Thermal properties		(wt.%)	(°C)
	PI	MMT	T_5 (°C)[a]	T_{10} (°C)[b]	Char yield (%)[c]	LOI
PI	100	0	400	445	32	30/3
PCN1	99	1	280	420	48	36/7
PCN5	95	5	420	455	43	34/5

[a,b]Temperature at which 5% or 10% weight loss was recorded TGA at a heating rate of 10°C/min in N_2.
[c]Weight percentage of material left after TGA analysis at maximum temperature 800°C in N_2.

4 Conclusions

A series of PI and PCNs consisting of organoclay were prepared by effectively dispersing the organoclay in an organic PI matrix by a solution intercalation. The synthesized PI and PCNs were characterized by FTIR, wide-angle powder XRD, and SEM. The effects of material composition on thermal stability of PI and PCNs were studied by TGA. Dispersal of organoclay into the PI matrix was found to boost the thermal stability as by the enhancement of thermal properties of the PI based on the TGA studies.

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